STIC Search Report
EIC 1700

STIC Database Tracking Number: 175384

TO: Ben Sackey
Location: REM 5B31
Art Unit : 1626
January 10, 2006

Case Serial Number: 10/719856

From: Kathleen Fuller
Location: EIC 1700
REMSEN 4B28
Phone: 571/272-2505
Kathleen.Fuller@uspto.gov

Search Notes

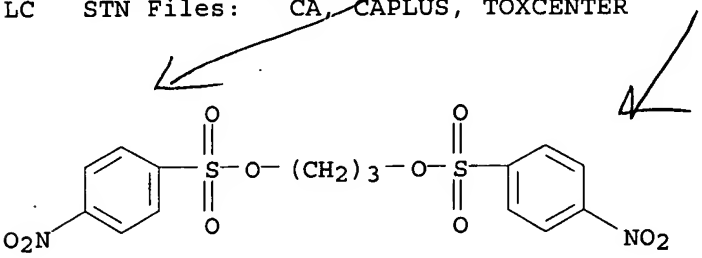
I think the applicants were blowing smoke with their nomenclature for the compound in claim 1- DNTDFD or that dinosyl part of the name. I finally figured out what the structure was –see the attachments. There were only 3 references in Casreact and 2 in CA.

Protonitronium. See, *Synthesis and Structure of HNFX*, Robert D. Chapman, Journal of Organic Chemistry (1999, 64, 960-965).

The known methods for producing DNTDFD are described in *Difluoramination of Heterocyclic Ketones: Control of Microbasicity* , Robert D. Chapman, Journal of Organic Chemistry (1998, 63, 1566). The compound HNFX is similar to another explosive and propellant oxidizer, TNFX. The process of preparing TNFX is detailed in U.S. Patent Application No. 2000/0161248, to Chapman and in U.S. Patent No. 6,417,355, also to Chapman. The precursor to TNFX is a compound very similar to DNTDFD. Both compounds are synthesized by a lengthy process requiring fluctuating temperature conditions. In preparing the precursor to TNFX, the reaction proceeds slowly and must be encouraged by cycling the temperature between -15 degrees C and 0 degrees C throughout the process, which reaches completion in two weeks time.

The process of preparing DNTDFD, as described in *Difluoramination of Hetrerocyclic Ketones: Control of Microbasicity*, Robert D. Chapman, Journal of Organic Chemistry (1998, 63, 1566 at 1570), requires a solution of fuming sulfuric acid, to which CH_2Cl_2 is added and cooled to -15 degrees C. Gaseous HNF_2 is absorbed into the layer of CH_2Cl_2. The temperature is raised, briefly, so that the HNF2, may be absorbed and the mixture is recooled. Tetrahydro-1,5-bis(4-nitrobenzenesulfonyl)-1,5-diazocine-3,7-(2H, 6H) dione is added to the mixture, which is stirred for 15 days. The solution is basified and precipitated. The product, DNTDFD, is obtained. During the course of the reaction, temperature is allowed to rise gradually from -15 degrees C to -8 degrees C. An alternate method is described, which involves the absorption of HNF_2 gas into a layer of FREON® 11 and the addition of tetrahydro - 1, 5-bis(4 -

L6 ANSWER 1 OF 2 REGISTRY COPYRIGHT 2006 ACS on STN
RN 25297-83-0 REGISTRY
ED Entered STN: 16 Nov 1984
CN Benzenesulfonic acid, 4-nitro-, 1,3-propanediyl ester (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN 1,3-Propanediol, bis(p-nitrobenzenesulfonate) (8CI)
CN Benzenesulfonic acid, p-nitro-, trimethylene ester (8CI)
OTHER NAMES:
CN **1,3-Propylene glycol dinosylate**
FS 3D CONCORD
MF **C15 H14 N2 O10 S2**
LC STN Files: CA, CAPLUS, TOXCENTER

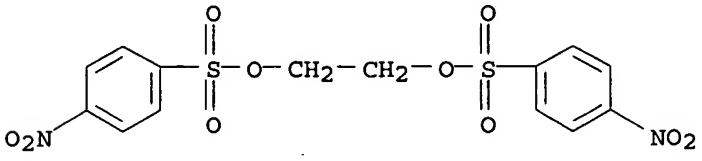


PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

3 REFERENCES IN FILE CA (1907 TO DATE)
3 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> D 2

L6 ANSWER 2 OF 2 REGISTRY COPYRIGHT 2006 ACS on STN
RN 25297-82-9 REGISTRY
ED Entered STN: 16 Nov 1984
CN Benzenesulfonic acid, 4-nitro-, 1,2-ethanediyl ester (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Benzenesulfonic acid, p-nitro-, ethylene ester (8CI)
CN Ethylene glycol, bis(p-nitrobenzenesulfonate) (8CI)
OTHER NAMES:
CN **Ethylene glycol dinosylate**
CN NSC 115800
FS 3D CONCORD
MF **C14 H12 N2 O10 S2**
LC STN Files: CA, CAPLUS, TOXCENTER



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ACCESS DB # 175384

PLEASE PRINT CLEARLY

Anvs: Fuller

Scientific and Technical Information Center

SEARCH REQUEST FORM

Requester's Full Name: BEN SACKEY Examiner #: 73489 Date: 12/30/05

Art Unit: 1626 Phone Number: 2-0200 Serial Number: 10/719,856

Location (Bldg/Room#): REM 5B31 (Mailbox #): Results Format Preferred (circle): (PAPER) DISK

To ensure an efficient and quality search, please attach a copy of the cover sheet, claims, and abstract or fill out the following:

Title of Invention: Process for Synthesizing 1,5-dinosyl-3,3,7,7-tetrakis(difluoramino) octahydro-1,5-diazocine) DNTD7D

Inventors (please provide full names): Adolph et al.

Earliest Priority Date: 11/24/03

Search Topic:

Please provide a detailed statement of the search topic, and describe as specifically as possible the subject matter to be searched. Include the elected species or structures, keywords, synonyms, acronyms, and registry numbers, and combine with the concept or utility of the invention. Define any terms that may have a special meaning. Give examples or relevant citations, authors, etc., if known.

For Sequence Searches Only Please include all pertinent information (parent, child, divisional, or issued patent numbers) along with the appropriate serial number.

4. process for prep. 1,5-dinosyl-3,3,7,7-tetrakis(difluoramino) octahydro-1,5 diazocine (DNTD7D) comprising reacting tetrahydro-1,5-bis(4-nitrobenzene sulfonyl)-1,5-diazocine-3,7 (2H,6H) dione with HNF_2/oleum in the presence of a diluent and absorbent for the reagent difluoramine.

Note diluent -> mixture of freon 11 with pentane, or cyclopentane or pentane alone

thanks

STAFF USE ONLY

Searcher: K. Fuller

Searcher Phone #:

Searcher Location:

Date Searcher Picked Up:

Date Completed: 1/10/06

Searcher Prep & Review Time: 40

Online Time: 60

Type of Search

NA Sequence (#)

AA Sequence (#)

2 Structure (#)

Bibliographic

Litigation

Fulltext

Other

Vendors and cost where applicable

✓ STN

Dialog

Questel/Orbit

Lexis/Nexis

Westlaw

WWW/Internet

In-house sequence systems

Commercial

Oligomer

Score/Length

Interference

SPDI

Encode/Transl

Other (specify)

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=> FILE REG
FILE 'REGISTRY' ENTERED AT 13:39:20 ON 10 JAN 2006
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
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Property values tagged with IC are from the ZIC/VINITI data file
provided by InfoChem.

STRUCTURE FILE UPDATES:    9 JAN 2006  HIGHEST RN 871542-42-6
DICTIONARY FILE UPDATES:   9 JAN 2006  HIGHEST RN 871542-42-6

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH JULY 14, 2005

  Please note that search-term pricing does apply when
  conducting SmartSELECT searches.

**********************************************************************
*                                                                    *
* The CA roles and document type information have been removed from *
* the IDE default display format and the ED field has been added,    *
* effective March 20, 2005.  A new display format, IDERL, is now     *
* available and contains the CA role and document type information.  *
*                                                                    *
**********************************************************************

Structure search iteration limits have been increased.  See HELP SLIMITS
for details.

REGISTRY includes numerically searchable data for experimental and
predicted properties as well as tags indicating availability of
experimental property data in the original document.  For information
on property searching in REGISTRY, refer to:

http://www.cas.org/ONLINE/UG/regprops.html

=> D L9

L9   ANSWER 1 OF 1  REGISTRY  COPYRIGHT 2006 ACS on STN
RN   202211-20-9  REGISTRY
ED   Entered STN:  05 Mar 1998
CN   1,5-Diazocine-3,3,7,7(2H,4H)-tetramine, N,N,N',N',N'',N'',N''',N'''-
     octafluorotetrahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI)  (CA INDEX
     NAME)
FS   3D CONCORD
MF   C18 H16 F8 N8 O8 S2
SR   CA
LC   STN Files:   CA, CAPLUS, CASREACT
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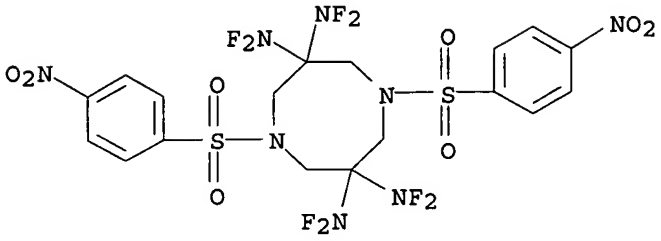


PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

2 REFERENCES IN FILE CA (1907 TO DATE)
2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

only 2 references

=> FILE HCAPLU
FILE 'HCAPLUS' ENTERED AT 13:39:40 ON 10 JAN 2006

FILE COVERS 1907 - 10 Jan 2006 VOL 144 ISS 3
FILE LAST UPDATED: 9 Jan 2006 (20060109/ED)

New CAS Information Use Policies, enter HELP USAGETERMS for details.

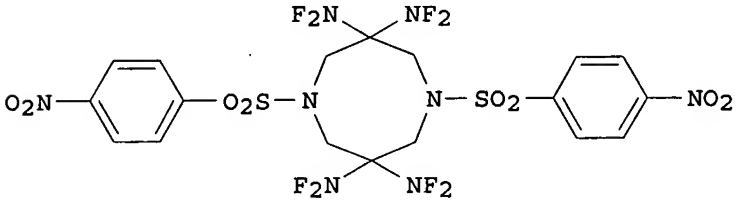
This file contains CAS Registry Numbers for easy and accurate substance identification.

=> D QUE
L9 1 SEA FILE=REGISTRY ABB=ON 202211-20-9
L10 2 SEA FILE=HCAPLUS ABB=ON L9

=> D L10 1-2 ALL

L10 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1999:30927 HCAPLUS
DN 130:209682
ED Entered STN: 18 Jan 1999
TI Nitrolysis of a highly deactivated amide by protonitronium. Synthesis and structure of HNFX
AU Chapman, Robert D.; Gilardi, Richard D.; Welker, Mark F.; Kreutzberger, Charles B.
CS Naval Aviation Science Technology Office, Naval Air Warfare Center Weapons

Division, China Lake, CA, 93555, USA
SO Journal of Organic Chemistry (1999), 64(3), 960-965
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 50, 75
OS CASREACT 130:209682
GI



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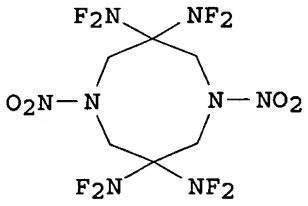

II

AB Efficient N-nitrolysis of the highly deactivated tetrakis(difluoramino)octahydrobis(4-nitrobenzenesulfonyl)diazocine I was achieved by the use of a protonitronium reagent formed in the system nitric acid-trifluoromethanesulfonic acid, producing tetrakis(difluoramino)octahydrodinitrodiazocine (II; HNFX) in 65% yield in a nonoptimized reaction. The crystal structure of the first morphol. of II contains cavities in the form of channels through its unit cell.

ST fluoroaminodiazocine bisnitrobenzenesulfonyl nitrolysis; nitrolysis protonitronium reagent nitrobenzenesulfonyldifluoroaminodiazocine; diazocine dinitrotetrakisdifluoroamino prepn mol crystal structure; HNFX prepn mol structure
IT Crystal structure
Molecular structure
(of tetrakis(difluoroamino)dinitrodiazocine)
IT Nitration
(preparation of tetrakis(difluoroamino)dinitrodiazocine by nitrolysis of bis(nitrophenylsulfonyl)diazocine derivative)
IT 170787-71-0P, HNFX
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)
IT 202211-14-1 **202211-20-9**
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)
IT 220841-48-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)

RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Achuthan, C; Propellants Explos Pyrotech 1990, V15, P271 HCAPLUS
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L10 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1998:157886 HCAPLUS
DN 128:140683
ED Entered STN: 17 Mar 1998
TI Difluoramination of Heterocyclic Ketones: Control of Microbasicity
AU Chapman, Robert D.; Welker, Mark F.; Kreutzberger, Charles B.
CS Research and Technology Group (Code 4B2200D), Naval Air Warfare Center Weapons Division, China Lake, CA, 93555, USA
SO Journal of Organic Chemistry (1998), 63(5), 1566-1570
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 50
OS CASREACT 128:140683
AB Difluoramination of a tetrahydro-1,5-diazocine-3,7(2H,6H)-dione to the corresponding 3,3,7,7-tetrakis(difluoramino)diazocine was achieved by a judicious choice of protecting group. Arenesulfonyl protecting groups for

This reference is cited in the specifications p2 as a prep for DNTDFD though it does not call it that.

the diazocine nitrogens proved superior to acetyl during the slow disruption of the transannular bridge in 9-oxa-3,7-diazabicyclo[3.3.1]nonane intermediates by difluorosulfamic acid. While a 1,5-ditosyl derivative failed to proceed beyond the product of addition of difluoramine to one ketone carbonyl, the use of 4-nitrobenzenesulfonyl as the protecting groups lowered the nitrogens' basicities below that of the oxygen site in the dione and intermediates, allowing the reaction to proceed to a gem-bis(difluoramino)diazocine product. A safer procedure for handling difluoramine is described.

ST tetrahydrodiazocinedione difluoramination; diazocinedione tetrahydro difluoramination; difluoramination heterocyclic ketone; safety handling difluoramine

IT Amination
(difluoramination of tetrahydrodiazocinedione)

IT Protective groups
(effect of protecting groups in difluoramination of tetrahydrodiazocinedione)

IT Safety
(in handling difluoramine)

IT 106-89-8, reactions 1510-31-2 6325-93-5 94683-14-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

IT 10405-27-3P, Difluoramine 160624-80-6P 202211-14-1P 202211-16-3P 202211-17-4P 202211-18-5P 202211-19-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

IT 202211-15-2P **202211-20-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(difluoramination of tetrahydrodiazocinedione)

RE.CNT 42 THERE ARE 42 CITED REFERENCES AVAILABLE FOR THIS RECORD

RE

(1) Axenrod, T; J Org Chem 1995, V60, P1959 HCAPLUS
(2) Baum; Final report to the Office of Naval Research (Arlington, VA) on Contract N00014-88-C-0536 1991, ONR-7-1
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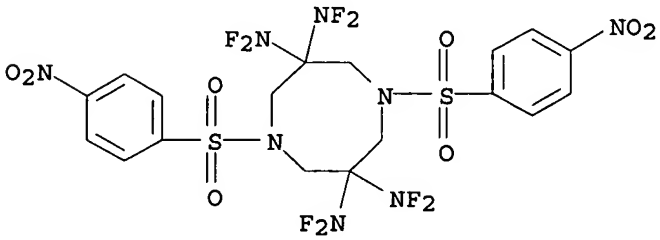
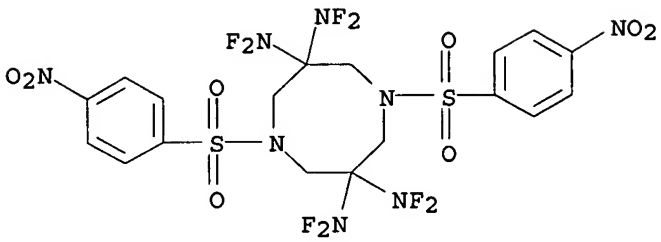
=> D L10 TI HITSTR 1-2 structures for above 2 references

L10 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
TI Nitrolysis of a highly deactivated amide by protonitronium. Synthesis and structure of HNFX
IT **202211-20-9**
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)
RN 202211-20-9 HCAPLUS
CN 1,5-Diazocine-3,3,7,7(2H,4H)-tetramine, N,N,N',N',N'',N'',N''',N'''-octafluorotetrahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



L10 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
TI Difluoramination of Heterocyclic Ketones: Control of Microbasicity
IT **202211-20-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(difluoramination of tetrahydrodiazocinedione)
RN 202211-20-9 HCAPLUS
CN 1,5-Diazocine-3,3,7,7(2H,4H)-tetramine, N,N,N',N',N'',N'',N''',N'''-octafluorotetrahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



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FILE CONTENT:1840 - 8 Jan 2006 VOL 144 ISS 2

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****
*
* CASREACT now has more than 10 million reactions *
*
****

Some CASREACT records are derived from the ZIC/VINITI database (1974-1991) provided by InfoChem, INPI data prior to 1986, and Biotransformations database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance identification.

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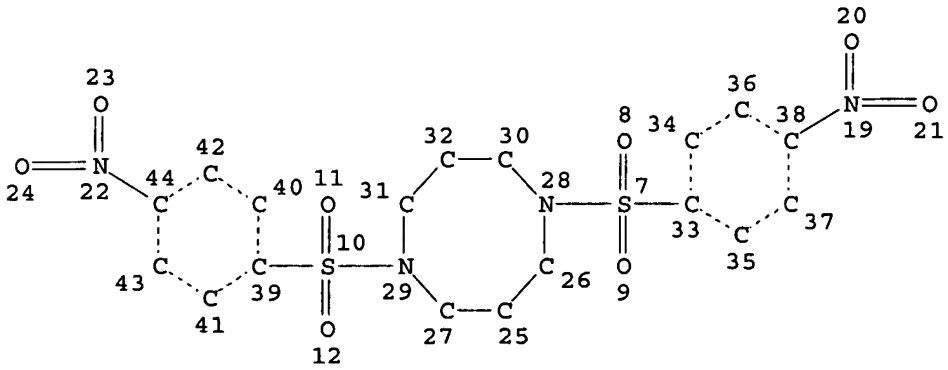
L11 STR



any reaction with this

NODE ATTRIBUTES:
DEFAULT MLEVEL IS ATOM

DEFAULT ECLEVEL IS LIMITED

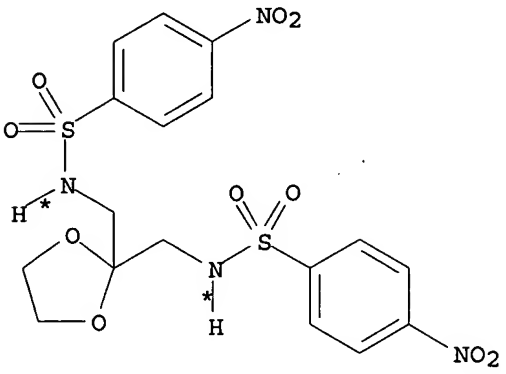
GRAPH ATTRIBUTES:
RING(S) ARE ISOLATED OR EMBEDDED
NUMBER OF NODES IS 32

STEREO ATTRIBUTES: NONE
L13 3 SEA FILE=CASREACT SSS FUL L11 (52 REACTIONS)

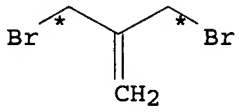
=> D L13 FHIT BIB ABS IND

L13 ANSWER 1 OF 3 CASREACT COPYRIGHT 2006 ACS on STN

RX(4) OF 100 ...J + M ===> **N**...



J



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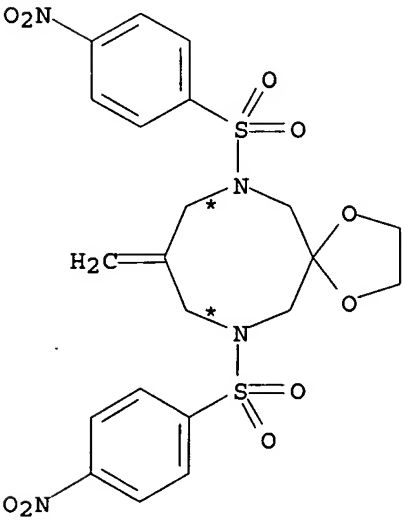


N
YIELD 76%

RX(4) RCT J 333421-17-3, M 15378-31-1
RGT O 584-08-7 K2CO3
PRO N **333421-21-9**
SOL 67-64-1 Me2CO

AN 137:78873 CASREACT

TI Preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers

IN Chapman, Robert Dale; Axenrod, Theodore; Sun, Jianguang; Guan, Xiao-Pei; Qi, Lida

PA United States Dept. of the Navy, USA

SO U.S., 12 pp.
CODEN: USXXAM

DT Patent

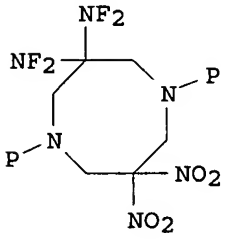
LA English

FAN.CNT 1

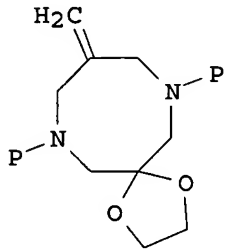
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI US 6417355	B1	20020709	US 2001-835783	20010411
US 2002161248	A1	20021031	US 2002-166278	20020603
US 6562985	B2	20030513		
PRAI US 2001-835783	20010411			

OS MARPAT 137:78873

GI



I



II

AB Disclosed is a process for the preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine [I; P = NO2]. Intermediate II [prepared in 4 steps; P = 4-nitrobenzenesulfonyl] subjected to the following steps: i. CH2Cl2, O3, -78°C/Me2S; ii. EtOH, NH2OH•HCl, NaOAc, reflux; iii. CH2Cl2, HNO3/NH4NO3/urea, reflux; iv. CH2Cl2, H2SO4 and v. CFCl3, H2SO4, HNF2, -25° → 10° → -15°, 3 h to produce, after aqueous work-up, the acetone solvate of I (explosive; P = 4-nitrobenzenesulfonyl; III). III was converted to I by treatment with CF3SO3H, HNO3, at 55° and aging the mixture for 14 days followed by addition of SbF5. Removal of triflic acid by distillation followed by aqueous work-up yielded the title compound I provides a difluoroamino component desired for energetic combustion of metalized-fuel propellant formulations, and the gem-dinitro component provides higher oxygen balance (for more-complete combustion) than analogous all-difluoroamino derivs.

IC ICM C07D225-04
ICS C07D245-00

NCL 540466000

CC 27-21 (Heterocyclic Compounds (One Hetero Atom))
Section cross-reference(s): 50

ST safety geminal dinitro diazocine explosion difluoroamino propellant combustion

IT Combustion

Explosion
Explosives
Nitration
Propellants (fuels)
(preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers)

IT Lewis acids
RL: RGT (Reagent); RACT (Reactant or reagent)
(preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers)

IT Nitramines
RL: SPN (Synthetic preparation); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers)

IT 193021-35-1P
RL: SPN (Synthetic preparation); TEM (Technical or engineered material use); PREP (Preparation); USES (Uses)
(combustible, explosive; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers)

IT 440651-48-9P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate, explodes!; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX) and related intermediates)

IT 333421-07-1P 333421-09-3P 333421-11-7P 333421-13-9P 333421-15-1P
333421-17-3P 333421-19-5P 333421-21-9P 333421-23-1P 333421-25-3P
333421-27-5P 333421-29-7P 333421-31-1P 333421-33-3P 333421-35-5P
333421-36-6P 333421-37-7P 440651-52-5P 440651-53-6P,
Hexahydro-7,7-dinitro-1,5-bis(3-fluorobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-54-7P, Hexahydro-7,7-dinitro-1,5-bis(4-fluorobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-55-8P, Hexahydro-7,7-dinitro-1,5-bis(2-cyanobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-56-9P,
Hexahydro-7,7-dinitro-1,5-bis(3-cyanobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-57-0P, Hexahydro-7,7-dinitro-1,5-bis(4-cyanobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-58-1P, Hexahydro-7,7-dinitro-1,5-bis(3-nitrobenzenesulfonyl)-1,5-diazocin-3(2H)-one 440651-59-2P,
3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(2-fluorobenzenesulfonyl)-1,5-diazocine 440651-60-5P, 3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(3-fluorobenzenesulfonyl)-1,5-diazocine 440651-61-6P, 3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(4-fluorobenzenesulfonyl)-1,5-diazocine 440651-62-7P,
3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(2-cyanobenzenesulfonyl)-1,5-diazocine 440651-63-8P, 3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(3-cyanobenzenesulfonyl)-1,5-diazocine 440651-64-9P, 3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(4-cyanobenzenesulfonyl)-1,5-diazocine 440651-65-0P,
3,3-Bis(difluoroamino)octahydro-7,7-di(nitro)-1,5-bis(3-nitrobenzenesulfonyl)-1,5-diazocine 440651-66-1P 440651-67-2P
440651-68-3P 440651-69-4P 440651-70-7P 440651-71-8P 440651-72-9P
440651-73-0P 440651-74-1P 440651-75-2P 440651-76-3P 440651-77-4P
440651-78-5P 440651-79-6P 440651-80-9P 440651-81-0P 440651-82-1P
440651-83-2P 440651-84-3P 440651-85-4P 440651-86-5P 440651-87-6P
440651-88-7P 440651-89-8P 440651-90-1P 440651-91-2P 440651-92-3P
440651-93-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT

(Reactant or reagent)
(intermediate; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX) and related intermediates)

IT 333421-34-4P, Hexahydro-7,7-di(nitro)-1,5-bis(2-nitrobenzenesulfonyl)-1,5-diazocin-3(2H)-one
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(intermediate; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX), related intermediates and use in explosives and propellant oxidizers)

IT 7783-70-2, Antimony pentafluoride 64371-01-3, Boron triflate 440651-94-5
RL: RGT (Reagent); RACT (Reactant or reagent)
(nitration catalyst; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX) and related intermediates)

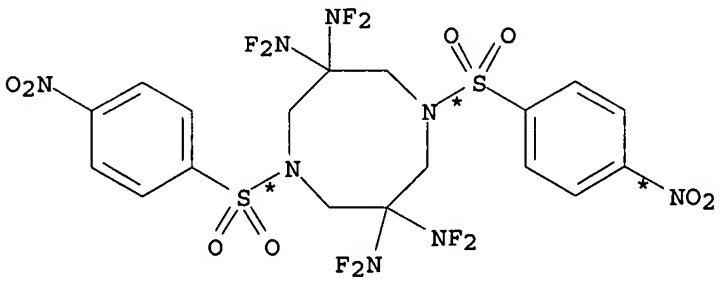
IT 98-74-8, p-Nitrobenzenesulfonyl chloride 616-29-5 1694-92-4, 2-Nitrobenzenesulfonyl chloride 15378-31-1, 3-Bromo-2-(bromomethyl)propene
RL: RCT (Reactant); RACT (Reactant or reagent)
(reactant; preparation of 3,3-bis(difluoroamino)octahydro-1,5,7,7-tetra(nitro)-1,5-diazocine (TNFX) and related intermediates)

RE.CNT 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> D L13 FHIT BIB ABS IND 2-3

L13 ANSWER 2 OF 3 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 1 **A** ===> B



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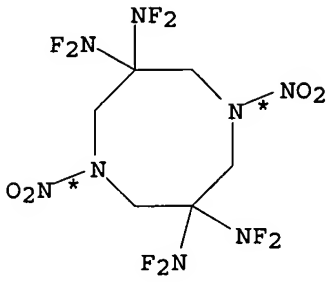
A



B
YIELD 65%

RX(1) RCT A **202211-20-9**
RGT C 7697-37-2 HNO3, D 1493-13-6 F3CSO2H
PRO B 170787-71-0

AN 130:209682 CASREACT

TI Nitrolysis of a highly deactivated amide by protonitronium. Synthesis and structure of HNFX

AU Chapman, Robert D.; Gilardi, Richard D.; Welker, Mark F.; Kreutzberger, Charles B.

CS Naval Aviation Science Technology Office, Naval Air Warfare Center Weapons Division, China Lake, CA, 93555, USA

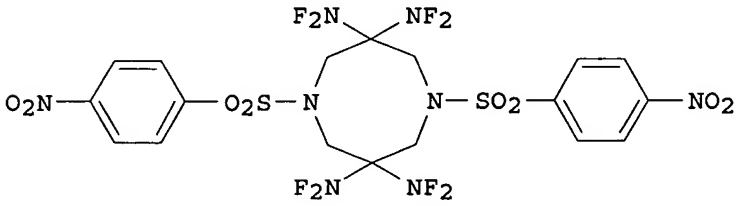
SO Journal of Organic Chemistry (1999), 64(3), 960-965
CODEN: JOCEAH; ISSN: 0022-3263

PB American Chemical Society

DT Journal

LA English

GI



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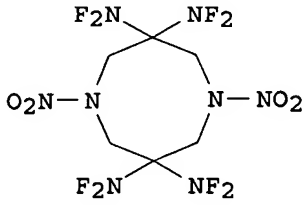


II

AB Efficient N-nitrolysis of the highly deactivated tetrakis(difluoramino)octahydrobis(4-nitrobenzenesulfonyl)diazocine I was achieved by the use of a protonitronium reagent formed in the system nitric acid-trifluoromethanesulfonic acid, producing tetrakis(difluoramino)octahydrodinitrodiazocine (II; HNFX) in 65% yield in a nonoptimized reaction. The crystal structure of the first morphol. of

II contains cavities in the form of channels through its unit cell.

CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 50, 75

ST fluoroaminodiazocine bisnitrobenzenesulfonyl nitrolysis; nitrolysis protonitronium reagent nitrobenzenesulfonyldifluoroaminodiazocine; diazocine dinitrotetrakisdifluoroamino prepn mol crystal structure; HNFX prepn mol structure

IT Crystal structure
Molecular structure
(of tetrakis(difluoroamino)dinitrodiazocine)

IT Nitration
(preparation of tetrakis(difluoroamino)dinitrodiazocine by nitrolysis of bis(nitrophenylsulfonyl)diazocine derivative)

IT 170787-71-0P, HNFX
RL: PRP (Properties); SPN (Synthetic preparation); PREP (Preparation)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)

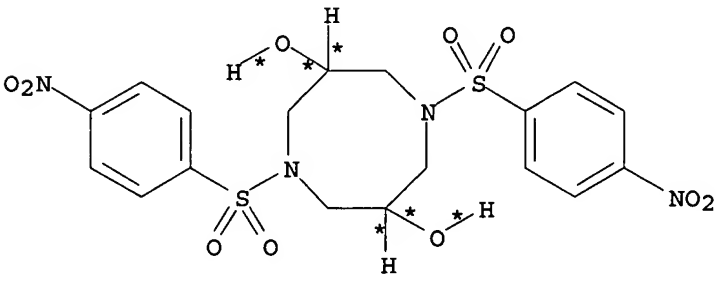
IT 202211-14-1 202211-20-9
RL: RCT (Reactant); RACT (Reactant or reagent)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)

IT 220841-48-5P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(preparation and mol./crystal structure of tetrakis(difluoroamino)dinitrodiazocine)

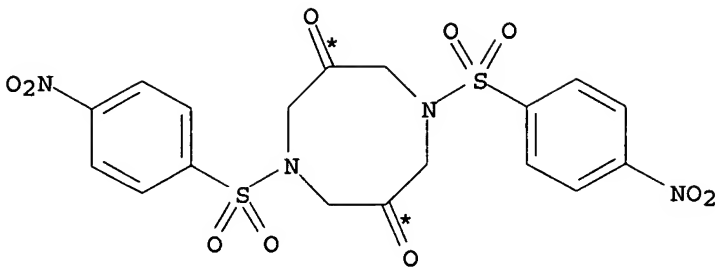
RE.CNT 35 THERE ARE 35 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L13 ANSWER 3 OF 3 CASREACT COPYRIGHT 2006 ACS on STN

RX(1) OF 6 ...**A** ===> B...



A (1) ⟶



B
YIELD 94%

RX(1) RCT A **202211-16-3**

STAGE(1)
RGT C 67-68-5 DMSO
SOL 75-09-2 CH2Cl2

STAGE(2)
RGT D 79-37-8 (COCl)2
SOL 75-09-2 CH2Cl2

STAGE(3)
RGT E 121-44-8 Et3N

STAGE(4)
RGT F 7732-18-5 Water

PRO B 202211-17-4
NTE Swern oxidn.

AN 128:140683 CASREACT
TI Difluoramination of Heterocyclic Ketones: Control of Microbasicity
AU Chapman, Robert D.; Welker, Mark F.; Kreutzberger, Charles B.
CS Research and Technology Group (Code 4B2200D), Naval Air Warfare Center Weapons Division, China Lake, CA, 93555, USA
SO Journal of Organic Chemistry (1998), 63(5), 1566-1570
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
AB Difluoramination of a tetrahydro-1,5-diazocine-3,7(2H,6H)-dione to the corresponding 3,3,7,7-tetrakis(difluoramino)diazocine was achieved by a judicious choice of protecting group. Arenesulfonyl protecting groups for the diazocine nitrogens proved superior to acetyl during the slow disruption of the transannular bridge in 9-oxa-3,7-diazabicyclo[3.3.1]nonane intermediates by difluorosulfamic acid. While a 1,5-ditosyl derivative failed to proceed beyond the product of addition of difluoramine to one ketone carbonyl, the use of 4-nitrobenzenesulfonyl as the protecting groups lowered the nitrogens' basicities below that of the oxygen site in the dione and intermediates, allowing the reaction to proceed to a gem-bis(difluoramino)diazocine product. A safer procedure for handling difluoramine is described.
CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 50
ST tetrahydrodiazocinedione difluoramination; diazocinedione tetrahydro

difluoramination; difluoramination heterocyclic ketone; safety handling difluoramine

IT Amination
(difluoramination of tetrahydrodiazocinedione)

IT Protective groups
(effect of protecting groups in difluoramination of tetrahydrodiazocinedione)

IT Safety
(in handling difluoramine)

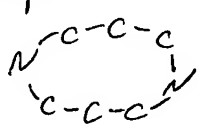
IT 106-89-8, reactions 1510-31-2 6325-93-5 94683-14-4
RL: RCT (Reactant); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

IT 10405-27-3P, Difluoramine 160624-80-6P 202211-14-1P 202211-16-3P 202211-17-4P 202211-18-5P 202211-19-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

IT 202211-15-2P 202211-20-9P
RL: SPN (Synthetic preparation); PREP (Preparation)
(difluoramination of tetrahydrodiazocinedione)

RE.CNT 42 THERE ARE 42 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

ring identifier for



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L15	364	SEA FILE=REGISTRY ABB=ON	L14 AND 46.150.18/RID
L16	143	SEA FILE=REGISTRY ABB=ON	L15 AND 3/NR
L17	53	SEA FILE=REGISTRY ABB=ON	L16 AND 2/S
L19	1	SEA FILE=REGISTRY ABB=ON	FLUORIMIDE/CN
L20	36	SEA FILE=HCAPLUS ABB=ON	L17
L21	267	SEA FILE=HCAPLUS ABB=ON	L19
L22	2	SEA FILE=HCAPLUS ABB=ON	L20 AND L21
L23	27	SEA FILE=HCAPLUS ABB=ON	L20(L)PREP/RL
L24	1	SEA FILE=REGISTRY ABB=ON	"FREON 11"/CN
L25	6602	SEA FILE=HCAPLUS ABB=ON	L24
L26	1	SEA FILE=HCAPLUS ABB=ON	L25 AND L23
L27	29	SEA FILE=HCAPLUS ABB=ON	L20 AND PREP/RL
L28	1	SEA FILE=HCAPLUS ABB=ON	L27 AND (FREON OR L25)
L29	2	SEA FILE=HCAPLUS ABB=ON	L22 OR L26 OR L28

=> D L29 BIB ABS IND HITSTR 1-2

L29 ANSWER 1 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 2001:222228 HCAPLUS
DN 134:282903
TI Synthesis of 3,3-bis(difluoramino)octahydro-1,5,7,7-tetranitro-1,5-diazocine (TNFX), a diversified energetic heterocycle
AU Axenrod, T.; Guan, X.-P.; Sun, J.; Qi, L.; Chapman, R. D.; Gilardi, R. D.
CS Department of Chemistry, The City College of the City University of New York, New York, NY, 100031, USA
SO Tetrahedron Letters (2001), 42(14), 2621-2623
CODEN: TELEAY; ISSN: 0040-4039
PB Elsevier Science Ltd.
DT Journal
LA English
AB The syntheses of new 3,3-dinitro derivs. of the 1,5-diazocine ring system are described. Highly deactivated precursor ketones hexahydro-7,7-dinitro-1,5-bis(2- and 4-nitrobenzenesulfonyl)-1,5-diazocin-3(2H)-ones were

difluoraminated to the corresponding gem-bis(difluoramino)diazocines. The 1,5-bis(4-nitrobenzenesulfonyl)diazocine derivative underwent N-nitrolysis with the protonitronium reagent formed in the nitric acid-trifluoromethanesulfonic acid-antimony pentafluoride system to produce 3,3-bis(difluoramino)octahydro-1,5,7,7-tetranitro-1,5-diazocine (TNFX), containing nitramine, gem-dinitro, and gem-bis(difluoramino) structural components.

CC 50-2 (Propellants and Explosives)
Section cross-reference(s): 28

ST TNFX fluoramino nitrodiazocine heterocyclic explosive; fluoramination gem nitration heterocycle explosive; nitramine fluoramino diazocine heterocycle explosive

IT Amination
(difluoroamination; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT Nitration
(gem-dinitration; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT Oxidation
Oximation
(in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT Explosives
(nitramine-type; synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT **75-69-4**, Trichlorofluoromethane 7664-93-9, Sulfuric acid, uses **10405-27-3**, Difluoroamine 41026-05-5, Sulfamic acid, difluoro-
RL: NUU (Other use, unclassified); USES (Uses)
(difluoramination reagent containing; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 1493-13-6, Trifluoromethanesulfonic acid 7697-37-2, Nitric acid, uses 7783-70-2, Antimony pentafluoride
RL: NUU (Other use, unclassified); USES (Uses)
(nitrating reagent containing; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 616-29-5, 1,3-Diamino-2-propanol
RL: RCT (Reactant); RACT (Reactant or reagent)
(nitrobenzenesulfonylation of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT **333421-36-6P 333421-37-7P**
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and deprotection-nitration of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT **333421-34-4P 333421-35-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and difluoramination of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-27-5P 333421-29-7P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and gem-dinitration of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-31-1P 333421-33-3P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and hydrolysis-deprotection of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-07-1P 333421-09-3P

RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and oxidation of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-23-1P 333421-25-3P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and oximation of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-11-7P 333421-13-9P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and protection of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

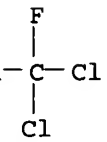
IT 333421-15-1P 333421-17-3P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and ring closure of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 193021-35-1P, 1,5-Diazocine-3,3(2H)-diamine, N,N,N',N'-tetrafluorohexahydro-1,5,7,7-tetranitro-
RL: SPN (Synthetic preparation); **PREP (Preparation)**
(synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT 333421-19-5P 333421-21-9P
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis of and ketone formation from; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

IT **75-69-4**, Trichlorofluoromethane **10405-27-3**, Difluoroamine
RL: NUU (Other use, unclassified); USES (Uses)
(difluoramination reagent containing; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

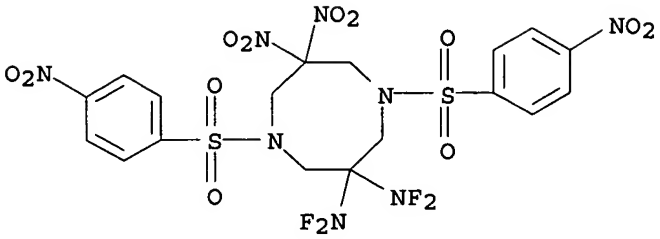
RN 75-69-4 HCAPLUS
CN Methane, trichlorofluoro- (8CI, 9CI) (CA INDEX NAME)



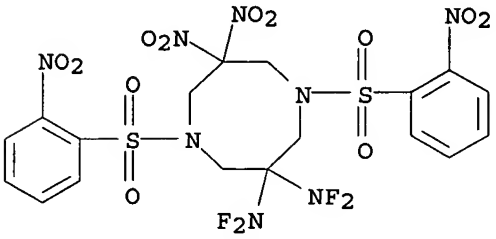
RN 10405-27-3 HCAPLUS
CN Fluorimide (6CI, 8CI, 9CI) (CA INDEX NAME)

IT **333421-36-6P 333421-37-7P**
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and deprotection-nitration of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)

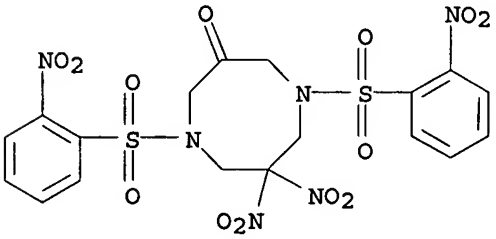
RN 333421-36-6 HCAPLUS
CN 1,5-Diazocine-3,3(2H)-diamine, N,N,N',N'-tetrafluorohexahydro-7,7-dinitro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



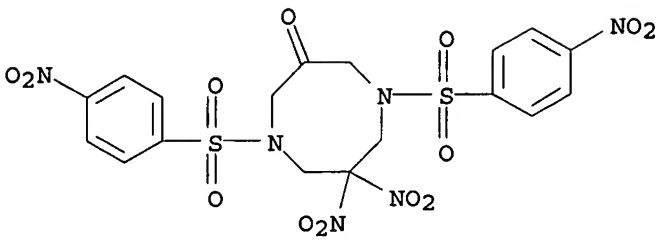
RN 333421-37-7 HCAPLUS
CN 1,5-Diazocine-3,3(2H)-diamine, N,N,N',N'-tetrafluorohexahydro-7,7-dinitro-1,5-bis[(2-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



IT **333421-34-4P 333421-35-5P**
RL: RCT (Reactant); SPN (Synthetic preparation); **PREP (Preparation)**; RACT (Reactant or reagent)
(synthesis and difluoramination of; in synthesis of TNFX, (difluoramino)tetranitrodiazocine, as novel energetic heterocycle)
RN 333421-34-4 HCAPLUS
CN 1,5-Diazocin-3(2H)-one, hexahydro-7,7-dinitro-1,5-bis[(2-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



RN 333421-35-5 HCAPLUS
CN 1,5-Diazocin-3(2H)-one, hexahydro-7,7-dinitro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



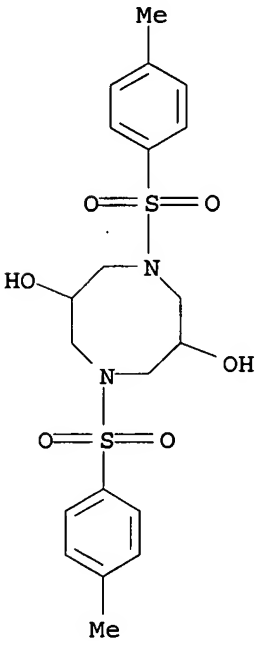
RE.CNT 24 THERE ARE 24 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L29 ANSWER 2 OF 2 HCAPLUS COPYRIGHT 2006 ACS on STN
AN 1998:157886 HCAPLUS
DN 128:140683
TI Difluoramination of Heterocyclic Ketones: Control of Microbasicity
AU Chapman, Robert D.; Welker, Mark F.; Kreutzberger, Charles B.
CS Research and Technology Group (Code 4B2200D), Naval Air Warfare Center Weapons Division, China Lake, CA, 93555, USA
SO Journal of Organic Chemistry (1998), 63(5), 1566-1570
CODEN: JOCEAH; ISSN: 0022-3263
PB American Chemical Society
DT Journal
LA English
OS CASREACT 128:140683
AB Difluoramination of a tetrahydro-1,5-diazocine-3,7(2H,6H)-dione to the corresponding 3,3,7,7-tetrakis(difluoramino)diazocine was achieved by a judicious choice of protecting group. Arenesulfonyl protecting groups for the diazocine nitrogens proved superior to acetyl during the slow disruption of the transannular bridge in 9-oxa-3,7-diazabicyclo[3.3.1]nonane intermediates by difluorosulfamic acid. While a 1,5-ditosyl derivative failed to proceed beyond the product of addition of difluoramine to one ketone carbonyl, the use of 4-nitrobenzenesulfonyl as the protecting groups lowered the nitrogens' basicities below that of the oxygen site in the dione and intermediates, allowing the reaction to proceed to a gem-bis(difluoramino)diazocine product. A safer procedure for handling difluoramine is described.
CC 28-23 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 50
ST tetrahydrodiazocinedione difluoramination; diazocinedione tetrahydro difluoramination; difluoramination heterocyclic ketone; safety handling difluoramine
IT Amination
(difluoramination of tetrahydrodiazocinedione)
IT Protective groups
(effect of protecting groups in difluoramination of tetrahydrodiazocinedione)
IT Safety
(in handling difluoramine)
IT 106-89-8, reactions 1510-31-2 6325-93-5 **94683-14-4**
RL: RCT (Reactant); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)
IT **10405-27-3P**, Difluoramine **160624-80-6P** 202211-14-1P
202211-16-3P **202211-17-4P** 202211-18-5P 202211-19-6P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

IT 202211-15-2P **202211-20-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(difluoramination of tetrahydrodiazocinedione)

IT **94683-14-4**
RL: RCT (Reactant); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

RN 94683-14-4 HCAPLUS
CN 1,5-Diazocine-3,7-diol, octahydro-1,5-bis[(4-methylphenyl)sulfonyl]- (9CI) (CA INDEX NAME)

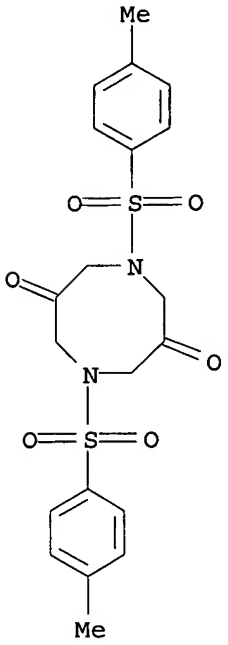


IT **10405-27-3P**, Difluoramine **160624-80-6P**
202211-16-3P 202211-17-4P
RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT (Reactant or reagent)
(difluoramination of tetrahydrodiazocinedione)

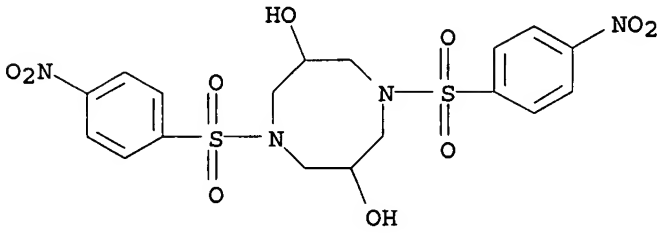
RN 10405-27-3 HCAPLUS
CN Fluorimide (6CI, 8CI, 9CI) (CA INDEX NAME)

F—NH—F

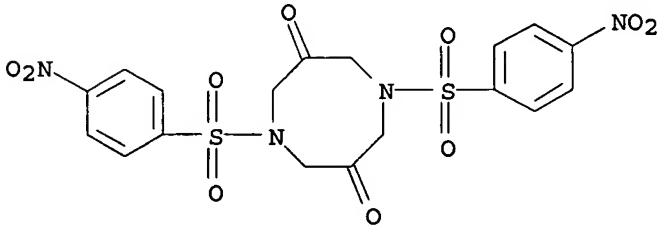
RN 160624-80-6 HCAPLUS
CN 1,5-Diazocine-3,7(2H,4H)-dione, tetrahydro-1,5-bis[(4-methylphenyl)sulfonyl]- (9CI) (CA INDEX NAME)



RN 202211-16-3 HCAPLUS
CN 1,5-Diazocine-3,7-diol, octahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)

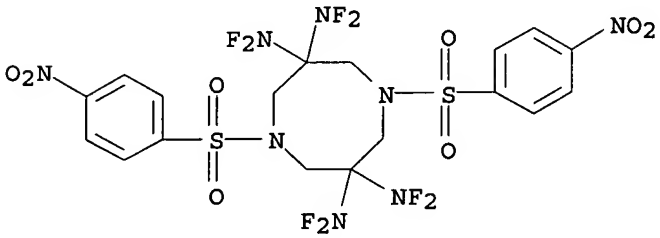


RN 202211-17-4 HCAPLUS
CN 1,5-Diazocine-3,7(2H,4H)-dione, tetrahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



IT **202211-20-9P**
RL: SPN (Synthetic preparation); PREP (Preparation)
(difluoramination of tetrahydrodiazocinedione)
RN 202211-20-9 HCAPLUS

CN 1,5-Diazocine-3,3,7,7(2H,4H)-tetramine, N,N,N',N',N'',N'',N''',N'''-octafluorotetrahydro-1,5-bis[(4-nitrophenyl)sulfonyl]- (9CI) (CA INDEX NAME)



RE.CNT 42 THERE ARE 42 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

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